Origin of Magnetism and trend in T_c in Cr-based double perovskites: Interplay of two driving mechanisms

Hena Das[1], Prabuddha Sanyal[1], T. Saha-Dasgupta[1,*], D.D. Sarma[2,†]

[1]*S.N. Bose National Centre for Basic Sciences, Kolkata 700098, India and*

[2] *Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India*

(Dated: January 25, 2011)

Employing first principles density functional calculations, together with solution of the low-energy, model Hamiltonian constructed in a first principles manner, we explored the origin of magnetism and T_c trend in Cr-based double perovskite series, $Sr_2CrB'O_6$ (B'=W/Re/Os). Our study shows that the apparently puzzling T_c trend in $Sr_2CrB'O_6$ (B'=W/Re/Os) series can be understood in terms of the interplay of the hybridization driven mechanism and the super-exchange mechanism.

I. INTRODUCTION

Oxides with high magnetic transition temperature (T_c) are important for technological advancement. A much discussed family of compounds in this connection are double perovskites, with a general formula $A_2BB'O_6$, A=alkaline/rare-earth metals and B/B'=transition metals. The observation[1] of large magnetoresistance with a fairly high ferromegnetic (FM) T_c of about 410 K in Sr_2FeMoO_6 (SFMO) and its unusual origin of magnetism brought this family of compounds into the forefront of activity. Since then the question has been, can T_c be boosted even further and if so, is there a systematic trend that can be observed and understood. Attempts have been made to dope SFMO with La to increase the T_c. Though some partial success has been achieved[2] following this path, T_c was found to be boosted much more efficiently by moving to different choices of B and B' ions. The microscopic understanding of this increase, however, has not been achieved. A collection of measured transition temperatures seems to bear some correlation with the number of valence electrons among different double perovskite compounds (see Fig.1 in Ref.3). Focusing onto Cr-based series, namely $Sr_2CrB'O_6$ (B' = W/Re/Os), the family with spectacularly high T_c, the measured T_c shows a rapid increase as one moves from Sr_2CrWO_6 (SCWO)[4] with $T_c \approx 450$ K to Sr_2CrReO_6 (SCRO)[5] with $T_c \approx 620$ K to Sr_2CrOsO_6 (SCOO)[6] with $T_c \approx 725$ K. This rapid increase is curious considering the hybridization driven (HD) mechanism[7,8] of magnetism accepted so far for double perovskites, proposed in the context of SFMO, which would predict decrease rather than the increase.[9]. Furthermore, the compound with the highest T_c in this series, SCOO, is found to be an insulator making the issue even more interesting. Also, a distinction between others like SFMO and La doped SFMO and this series is a possible role of spin-orbit coupling (SOC) due to the presence of 5d elements.

We have used density functional theory (DFT) based calculations together with exact diagonalization of Cr-B' model Hamiltonian constructed in a first-principles-derived Wannier function basis, in order to probe this issue. Though few DFT based studies[10] exist for individuals of these compounds, to best of our knowledge, theoretically no comprehensive study exists to address the origin of growing trend in T_c within the series.

II. METHODOLOGY

The DFT calculations were carried out using the plane wave pseudopotential method implemented within Vienna Ab-initio Simulation Package(VASP).[11] The exchange-correlation functionals were approximated by generalized gradient approximation (GGA).[12] We have used projected augmented wave (PAW) potentials[13] and the kinetic energy cut-off for expansion of wavefunctions used was 450 eV. Reciprocal space integrations have been carried out with a k-space mesh of 6×6×6. For extraction of a few-band, tight-binding Hamiltonian out of full GGA calculation, we have carried out muffin-tin orbital (MTO) based NMTO-downfolding calculations.[14] The reliability of the calculations in two basis sets has been cross-checked.

III. RESULTS

A. Examination of Basic Electronic Structure

In order to unravel the origin of magnetism in $Sr_2CrB'O_6$ series, let us first critically examine the electronic density of states (DOS) of these compounds. Left panel of Fig.1 shows the DOS, as obtained in spin-polarized DFT calculations within GGA. The states close to Fermi level (E_F) are dominated by Cr and B' d states hybridized with O p states, while the O p dominated states separated from Cr and B' d dominated states occupy the energy range far below E_F and Sr s and d dominated state remain far above E_F. The d states of Cr and the B' ions are exchange split as well as crystal field split. The empty B' t_{2g} states in the up-spin channel appear in between the crystal field split Cr t_{2g} and e_g states, gaped from E_F while the B' states in the down spin chan-
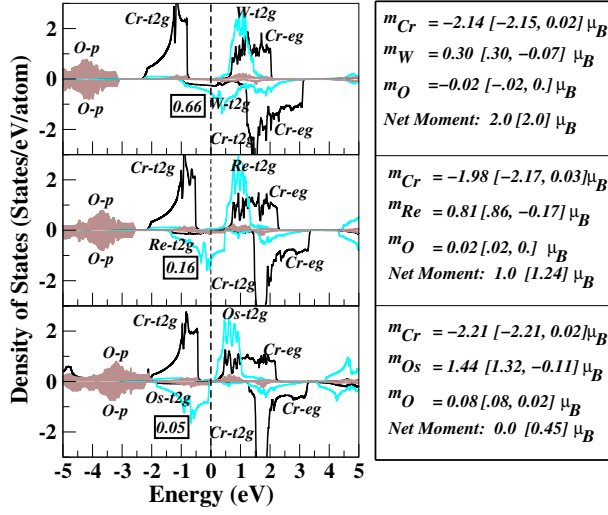
Figure 1: (Color online) Left Panels: GGA DOS projected onto Cr d (black solid lines), B$'$ d (Red/Grey solid lines) and O p (shaded area). Zero of the energy is set at E_F. The numbers within the boxes indicate the Cr t_{2g} contribution in the bands crossing E_F, with respect to that of B$'$. Right Panel: Calculated net magnetic moment and magnetic moments at Cr, B$'$ and O sites. The numbers within the bracket denote the result of GGA+SO calculations, the first entry being the spin moment and the second entry being the orbital moment. From top to bottom, the plots correspond to SCWO, SCRO and SCOO respectively.

Figure 2: (Color online) The energy level diagram (upper panel) and massively downfolded Wannier functions (lower panels) for $Sr_2CrB'O_6$ series. For Wannier function plots, constant value surfaces have been plotted with two oppositely signed lobes colored differently. From left to right in lower panel, the plots correspond to SCWO, SCRO and SCOO respectively. The numbers in the energy level diagram are in unit of eV.

B$'$ site following the dehybridization effect between Cr and B$'$.

nel hybridized with Cr t_{2g} states, either cross the Fermi level as in the case of W and Re compounds, or remain completely occupied, as in case of the Os compound. It is rather intriguing to notice that the hybridization between Cr t_{2g} and B$'$ t_{2g} in the down spin channel, progressively gets weakened in moving from W to Re to Os compound. This may be appreciated by considering the Cr contribution measured with respect to B$'$ contribution for the states in the down spin channel close to E_F. For W, Re and Os compounds, it is found to be 66%, 16 % and 5% respectively. This is caused by the gradual moving down of the B$'$ energy level, in moving from left to right of the periodic table across the same row (W $\rightarrow$ Re $\rightarrow$ Os), reflecting an increase in the ionic potential experienced by the 5d electrons with an increase in nuclear charge. As discussed later, the hopping interaction connecting Cr and B$'$ t_{2g} states on the other hand remains similar across the series. Analysing the DFT calculated magnetic moments, presented in the right panel of Fig.1, we find the second interesting observation that the magnetic moment per electron at B$'$ site, defined as m/d, where m is the calculated moment and d is the valence count at B$'$,[15] keeps growing from W to Re to Os. The increase in m/d becomes even more evident taking into account the magnetic moment at O site, which is small and point to Cr moment for SCWO, small (large) and point to Re (Os) moment for SCRO (SCOO). This prompts us to conclude that there is a growing intrinsic moment that develops at
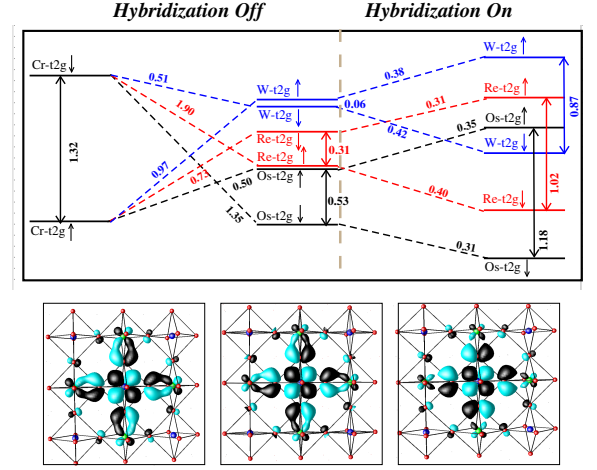
B. NMTO-downfolding calculations

In order to further analyse the findings of the electronic structure calculations, we have carried out NMTO downfolding calculations, which is engineered to define energy-selected, effective Wannier functions by integrating out degrees of freedom that are not-of-interest (*downfolding*). As a first step we downfolded O p, Sr as well as Cr and B$'$ e_g degrees of freedom. This defines an effective basis consisting of Cr t_{2g} and B$'$ t_{2g} states. In the second step, we applied massive downfolding, keeping only B$'$ t_{2g} degrees of freedom active and downfolding all the rest including Cr t_{2g} degrees of freedom. On site matrix elements of the real space Hamiltonian defined in the Cr t_{2g}-B$'$ t_{2g} basis and the massively downfolded basis give the energy level positions before and after switching on the hybridization between Cr and B$'$ states, respectively. Fig.2 summarizes the results for W, Re and Os compounds. The energy levels in the left and right half of the upper panel, demarked with vertical grey line, depict the energy level positions obtained out of downfolded Cr t_{2g}-B$'$ t_{2g} basis and the massively downfolded basis, respectively. The lower panels exhibit the plots of the one of the t_{2g} (xy) Wannier functions corresponding to massively downfolded Hamiltonian in the down spin channel. Examination of Fig.2 brings out two aspects: Firstly, the progressive dehybridization effect, as discussed in the context of DOS plots, is evident in the plots of Wannier functions. The central parts of the

Wannier functions are shaped according to B′ xy symmetry and the tails of the Wannier functions sitting at neighboring sites are shaped according to O p and Cr t_{2g} symmetry. The tails reflecting the hybridization between the Cr t_{2g} and B′ t_{2g}-O weaken as one moves from W to Re to Os compound. As a consequence, the ratio of renormalized spin splitting to that of the bare splitting at B′ site reduces drastically from W (14.5) to Re (3.3) to Os (2.2). Secondly, considering the level splitting at B′ site before switching on the hybridization, we find while the splitting at W is negligibly small confirming the non-magnetic character of the B′ site, those for Re and Os are found to be ≈ 0.31 eV and ≈ 0.53 eV, respectively. These values are significantly larger compared to what one would have expected considering d^2 valence in Re and d^3 valence in Os compared to d^1 valence in case of W with 0.06 eV splitting, which would have given rise to splittings of 0.12 eV and 0.18 eV respectively. This confirms the presence of a growing intrinsic, local moment at B′ site as one moves from W to Re to Os, driven by the dehybridization effect. The magnetism in Cr-B′ series, therefore, needs to be understood as an interplay of two mechanisms: HD mechanism as operative in SFMO which causes renormalized, negative spin splitting within B′ states that appear in between the exchange split Cr t_{2g} states, and the superexchange (SE) between the moment at Cr site and the intrinsic moment at B′ site, which would align the moments at Cr and B′ sites antiparallely. For W, the intrinsic moment being negligible, the magnetism is entirely driven by HD mechanism, while for the other extreme of Os, the hybridization effect is weak, SE having a rather large contribution. The presence of such intrinsic moment at 5d site is counterintuitive at a first glance. Comparing the situation, with the double perovskite Sr_2ScReO_6, for which the magnetism has been recently investigated,[16] Re was found to possess a rather small intrinsic moment of size 0.013 μ_B. Our electronic structure calculations carried out for Sr_2ScReO_6 find also a similarly small moment (0.03 μ_B). The unusual localized aspect of Re or Os, in case of Cr based compounds therefore arises due to the relative positioning of the Cr and B′ energy levels, which narrows down the width of the B′ states substantially in the up spin channel. The development of the intrinsic moment is thus helped by the delicate energy level structure responsible for the HD mechanism and would not have been present otherwise.

C. Total Energy Calculations

The calculations discussed so far, do not include SOC, which may be important. The numbers within the bracket in right panel of Fig.1 show the individual spin and orbital moments as well as net moments as obtained in GGA+SO calculations. As expected, the orbital moments are large at B′ site. Interestingly, we find while the net moment was zero for SCOO without SOC, it is the consideration of SOC that gives rise to a non-zero moment, due to the uncompensated orbital moment at B′ site. Whether SOC has any influence on the trend within the T_c's, therefore needs to be explored. Interplay of two driving mechanisms in W-Re-Os series, however, makes it difficult to extract the magnetic exchanges as energy difference between two specific magnetic configurations. The presence of finite, intrinsic moment at B′ site, as is the case for Re and Os compounds, makes the moment at B′ site frustrated in an antiferromagnetic (AFM) configuration of Cr spins. The finite presence of HD mechanism, on the other hand, disfavors stabilization of magnetic configurations with majority of B spins aligned parally to that of the moment at B′ site. Admitting these difficulties, we carried out total energy calculations of the two possible spin configurations, one FM arrangement and another A-type AFM arrangement of Cr spins, with Cr spins between two adjacent planes are antiferromagnetically coupled, and are ferromagnetically coupled in plane. For the AFM calculations, the moment at B′ site was found to be antiparallely (parallely) aligned to the spins of in-plane (out-of-plane) Cr sites which are four (two) in number. As expected, the energy differences between FM and AFM configurations are found to be positive for all cases proving FM arrangement of Cr spins to be the stable phase. The values of the energy difference is found to increase from W to Re system (from 0.23 eV/formula unit to 0.25 eV/formula unit), and then decrease from Re to Os system (from 0.25 eV/formula unit to 0.24 eV/formula unit). Introduction of SO interaction though changes the individual energy differences by about 0.03 eV, the trend remains unaltered. This indicates that although the presence of substantial SOC at B′ site is important for producing the large magneto-optical signals,[17] it plays little role in setting up the trend in T_c. In order to examine the role of missing correlation effect in GGA, we have also carried out LDA+U calculations with a choice of U value of 3 eV at Cr site and 0.8 eV at B′ site. Application of larger U at Cr site and relatively smaller one at B′ sites, as expected from the relative band-widths, were found to preserve the general conclusions intact with more localized character of d states at B′ site, as expected.

D. Exact Diagonalization Study of Model Hamiltonian

In view of the difficulty in stabilizing the appropriate excited state magnetic configuration, the stability of the FM arrangements of Cr spins may be measured as the energy difference between the FM spin configuration and the paramagnetic (PM) phase. The description of the PM phase needs consideration of different disordered spin configurations and averaging over a large number of them, which is almost impossible within the DFT framework. Such calculations are much easier to handle within a model Hamiltonian description. The model Hamiltonian, describing the interplay of the HD and SE mecha-

nism may be written as,

$$
\begin{aligned}
H =\ & \epsilon_{Cr} \sum_{i \in B} f^{\dagger}_{i\sigma\alpha} f_{i\sigma\alpha} + \epsilon_{B'} \sum_{i \in B'} m^{\dagger}_{i\sigma\alpha} m_{i\sigma\alpha} \\
& - t_{CB'} \sum_{<ij>\sigma,\alpha} f^{\dagger}_{i\sigma,\alpha} m_{j\sigma,\alpha} - t_{B'B'} \sum_{<ij>\sigma,\alpha} m^{\dagger}_{i\sigma,\alpha} m_{j\sigma,\alpha} \\
& - t_{CC} \sum_{<ij>\sigma,\alpha} f^{\dagger}_{i\sigma,\alpha} f_{j\sigma,\alpha} + J \sum_{i \in Cr} \mathbf{S}_i \cdot f^{\dagger}_{i\alpha} \vec{\sigma}_{\alpha\beta} f_{i\beta} \\
& + J_2 \sum_{i \in Cr, j \in B} \mathbf{S}_i \cdot \mathbf{s}_j
\end{aligned}
$$

where the f's and m's refer to the Cr t_{2g} and B' t_{2g} degrees of freedoms. $t_{CB'}$, $t_{B'B'}$, t_{CC} represent the nearest neighbor Cr-B', second nearest neighbor B'-B' and Cr-Cr hoppings respectively. σ is the spin index and α is the orbital index that spans the t_{2g} manifold. The difference between the ionic levels, $\Delta = \epsilon_{Cr} - \epsilon_{B'}$, defines the on-site energy difference between Cr t_{2g} and B' t_{2g} levels. s_j is the intrinsic moment at the B' site. The first, six terms of the Hamiltonian, represent the HD mechanism, which consist of a large core spin at the Cr site (S_i) and the coupling between the core spin and the itinerant electron delocalized over the Cr-B' network. Variants of this part has been considered by several authors[18–20] in the context of SFMO. The last term represents the SE mechanism, that consists of coupling between Cr spin and the intrinsic moment at B' site. The parameters of the model Hamiltonian are extracted out of DFT calculations through NMTO downfolding technique of constructing the real space Hamiltonian in the basis of effective Cr t_{2g} and B' t_{2g} degrees of freedom. $t_{CB'}$, $t_{B'B'}$ and t_{CC} hoppings are found to -0.35 eV, -0.12 eV and -0.08 eV respectively, with little variation within the W-Re-Os series. Δ-s show a varying trend within the W-Re-Os series ($\Delta^W = -0.66$ eV, $\Delta^{Re} = 0.03$ eV, $\Delta^{Os} = 0.26$ eV). The parameters involving J and J_2 were obtained from the spin-splitting at Cr site and the extra splitting observed at B' site as compared to that expected from the electron filling effect and the splitting for W compound.

The constructed model is then solved using exact diagonalization on a lattice of dimension $8 \times 8 \times 8$. Calculations have been carried out as well for lattices of size $4 \times 4 \times 4$ and $6 \times 6 \times 6$. The trend is found to be the same as presented for $8 \times 8 \times 8$. Exact diagonalization was first carried out considering the B' site to be totally nonmagnetic, *i.e.* setting the last term to zero, which boils down to the same underlying model Hamiltonian as that of SFMO. The energy difference between the PM and FM is found to decrease with increasing number of valence electron, as shown by diamond symbols in Fig.3. This is exactly the similar trend as found in a recent calculation on La doped SFMO,[21,22] as well as in Ref. 9 with FM getting destabilized with increase of valence electrons. This trend of suppression of T_c upon increasing valence electron count is further amplified due to change in Δ within the Cr-B' series. This variation in Δ in the present series is in contrast to the prescription given in ref.9 to achieve high T_c. Upon reaching
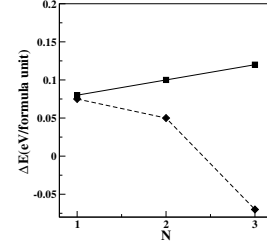

Figure 3: PM - FM energy differences plotted as a function of valence electron count, as obtained in exact diagonalization calculation. The diamond (square) symbols connected by dashed (solid) line correspond to calculations corresponding to Hamiltonian, without (with) J_2 term.

valence electron count equal to 3 which corresponds to Os compound, FM becomes totally unstable, reflected in negative sign of the energy difference. We note a rather rapid decrease in moving from N=2 case to N=3 case. This may reflect the special situation of Os compound, with Cr t^3_{2g}-B' t^3_{2g} configuration, an ideal super-exchange situation with insulating solution, that adds on to the general trend. The situation gets dramatically changed upon inclusion of the growing localized magnetic nature of the B' site, as shown by square symbols in Fig.3. Considering J_2 values, as obtained in GGA calculations, we find that PM and FM energy difference, recovers the correct trend in moving from W to Re to Os as has been observed experimentally. Mapping the PM and FM energy difference to the mean field T_c, one obtains values 870 K, 1160 K and 1450 K for the W, Re and Os compounds respectively. Although the values are overestimated compared to experimental values, presumably due to the finite size effect of exact diagonalization calculation and the mean field formula, the trend is very well reproduced with $T_c^{Re}/T_c^W = 1.33$ and $T_c^{Os}/T_c^{Re} = 1.25$, compared to experimental estimates of 1.38 and 1.17 respectively.[4–6]

IV. CONCLUSION AND DISCUSSION

In conclusion, we have studied the counter-intuitive T_c trend in Cr based double perovskites, $Sr_2CrB'O_6$ (B'=W/Re/Os). Analysis of the electronic and magnetic properties shows that the progressive enhancement of the T_c across the 5d series should be understood as the interplay of two driving mechanisms: HD mechanism responsible for the negative spin splitting at B' site as in SFMO, and SE mechanism. The HD mechanism gets weaker as one moves along the series from W to Re to Os, due to the increased energy level separation of B' from Cr. SE, on the other hand, gets stronger in moving from SCWO to SCRO to SCOO due to the presence of growing intrinsic moment at B' site, following the dehybridization effect. The observation of uncompensated moment in SCOO arises due to the presence of SO. SCOO, in that sense, should be thought as a ferrimagnet rather than a ferromagnet. With this, we demystify the puzzling T_c

trend in Cr-B′ double perovskite series.

knowledges discussion with L. Alff.

∗ tanusri@bose.res.in † sarma.dd@gmail.com

[1] K.-I. Kobayashi, T. Kimura, H. Sawada, K. Terakura, and Y. Tokura, Nature (London) **395**, 677 (1998).

[2] J. Navarro, J. Fontcuberta, M. Izquierdo, J. Avila, and M. C. Asensio, Phys. Rev. B **69**, 115101 (2004); C. Frontera, D. Rubía, J. Navarroa, J. L. García-Muñoza, C. Ritterb and J. Fontcuberta, Physica B **350**, e285 (2004).

[3] Tapas Kumar Mandal, Claudia Felser, Martha Greenblatt, and Jürgen Kübler, Phys. Rev. B **78**, 134431 (2008).

[4] J.B. Phillip *et. al.*, Phys. Rev.B, **68**, 144431 (2003).

[5] H. Kato, T. Okuda, Y. Okimoto, Y. Tomioka, Y. Takenoya, A. Ohkubo, M. Kawasaki, and Y. Tokura, App. Phys. Lett **81**, 328 (2002).

[6] Y. Krockenberger, K. Mogare, M. Reehuis, M. Tovar, M. Jansen, G. Vaitheeswaran, V. Kanchana, F. Bultmark, A. Delin, F. Wilhelm, A. Rogalev, A. Winkler, and L. Alff, Phys. Rev. B **75**, 020404 (2007).

[7] D. D. Sarma, Priya Mahadevan, T. Saha-Dasgupta, Sugata Ray, and Ashwani Kumar, Phys. Rev. Lett. **85**, 2549 (2000).

[8] J. Kanamori and K. Terakura, J. Phys. Soc. Jpn. **70**, 1433 (2001).

[9] A. Chattopadhyay and A. J. Millis, Phys. Rev. B **64**, 024424 (2001)

[10] H. Jeng and G. Y. Guo, Phys. Rev B **67**, 094438 (2003); Vaitheeswaran *et al.*, Appl. Phys. Lett. **86**, 032513 (2005); K. -W. Lee and W. Pickett, Phys. Rev. B **77**, 115101 (2007).

[11] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).

[12] J. P. Perdew *et. al.*, Phys. Rev. B **48**, 4978(E) (1993).

[13] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).

[14] O. K. Andersen and T. Saha-Dasgupta, Phys. Rev. B **62**, R16219 (2000).

[15] The nominal 5^+ valence state corresponds to $5d^1$, $5d^2$, $5d^3$ configuration of W, Re and Os respectively.

[16] A Winkler, N Narayanan, D Mikhailova, K G Bramnik, H Ehrenberg, H Fuess, G Vaitheeswaran, V Kanchana, F Wilhelm, A Rogalev, A Kolchinskaya and L Alff, New J Phys **11** 073047 (2009).

[17] H. Das, M. De-Raychaudhury and T. Saha-dasgupta, Appl. Phys. Lett. **92**, 201912 (2008).

[18] J. L. Alonso, L. A. Fernández, F. Guinea, F. Lesmes, and V. Martín-Mayor, Phys. Rev. B, **67**, 214423 (2003).

[19] O. Navarro, E. Carvajal, B. Aguilar, M. Avignon, Physica B **384**, 110 (2006).

[20] L. Brey, M. J. Calderón, S. Das Sarma, and F. Guinea, Phys. Rev. B **74**, 094429 (2006).

[21] P. Sanyal, H. Das and T. Saha-Dasgupta, Phys. Rev. B **80**, 224412 (2009).

[22] The experimental observation of increase of T_c upon La doping in SFMO may be rationalized in terms of the increase of the antisite disorder as predicted in Ref.18.